Production of Solar Grade Silicon by Refining of Liquid Metallurgical Grade Silicon

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ABSTRACT

A simple boron (B) reduction process has been developed to reduce B to 0.3 ppma for metallurgical grade (MG) silicon and <1 ppma for heavily B-doped electronic scrap. This simple, direct reduction process is a technical breakthrough and a vital step towards solar grade (SoG) silicon production. Solar cells fabricated using refined electronic scrap were comparable to cells produced using electronic grade silicon feedstock.

1. Introduction

In 1999, the photovoltaic (PV) industry became a billion dollar industry with the production of over 200 MW of modules. Recently, the industry is growing at an annual rate of between 25 and 40 percent[1]. The PV Industry Roadmap estimates[2] that with a 25% and 30% growth rate between 2000 and 2020 the total worldwide shipments of PV modules will be 7 and 15 GW per year, respectively. Addressing new electrical generating requirements, for the domestic PV industry to provide up to 15% of the new U.S. peak electricity generating capacity required by 2020, the PV modules requirement will be 30 GW.

Within the PV industry, crystalline silicon is the most developed material and accounts for most of the commercial modules used for power generation. In 2000, 288 MW of PV modules were produced worldwide, of which 258 MW were crystalline silicon. The remainder consisted of amorphous silicon and thin-film technologies. One of the justifications for thin-film technologies is that the conventional crystalline silicon PV modules use a high-cost silicon feedstock that is available in limited quantity.

It is recognized that the purity requirements of silicon feedstock for solar cell application are less demanding than those for the electronic industry but a lower grade silicon is not commercially available. The lack of availability of low-cost solar grade (SoG) silicon is the biggest problem that can impede the future growth of the PV industry.

Upgrading metallurgical grade (MG) silicon has been an attractive approach, but reducing boron (B) and phosphorus (P) to <1 ppma has been a problem. Several approaches have been tried, but none have reached commercialization. Refining of commercially available, as-received MG silicon in the molten state was carried out using a modified HEM furnace[3-5]. B was reduced to 0.3 ppma and P to 7 ppma from original levels of 40-60 ppma. The B reduction process was applied to heavily B-doped electronic scrap. For the scrap, B levels were reduced to <1 ppma and refined material was used as feedstock.

Development of a simple B-reduction process is a technical breakthrough and a vital step towards SoG production. This process applied to electronic scrap will immediately make available a new feedstock source for another 200 MW per year of module production by the PV industry.

2. Boron-Reduction Process

To develop cost effective upgrading of MG silicon, it is important that minimal steps are used and that the selected processes are integrated and compatible with large-scale production. In 1980, a small R&D effort was initiated to show feasibility of a simple approach for upgrading MG silicon. It was recognized that directional solidification is effective for reduction of most impurities and that only one directional solidification step is necessary to segregate impurities and minimize costs. However, B and P have to be refined using simple processing in the molten state prior to directional solidification. It was also clear that different grinding and leaching steps of purification did not lend themselves to a cost-effective approach. The scenario envisioned was to pour molten MG silicon from the arc furnace into a refining unit where B and P would be initially removed and the refined silicon then directionally solidified. To achieve this goal, the B and P refining process had to be compatible with the process and facilities of an MG silicon production plant. The R&D work started in 1980 showed the feasibility of upgrading MG silicon so that all metallic impurities were <1 ppm[6].

Under a PVMaT program initiated in 1998, systematic processes were developed with the same approach of refining B and P in the molten MG silicon followed by directional solidification[3-5]. A schematic of this approach is shown in Figure 1.

The refining process involved moist gas blowing through molten silicon. After the refining step, the melt was directionally solidified. It was shown that, except for B and P, other impurities were reduced to < 0.1 ppma[4]. In an effort to show that the B concentration can be reduced to <1 ppma by refining commercially-available MG silicon, refining experiments were carried out. After the refining step the melt was solidified without pursuing a good directional solidification.

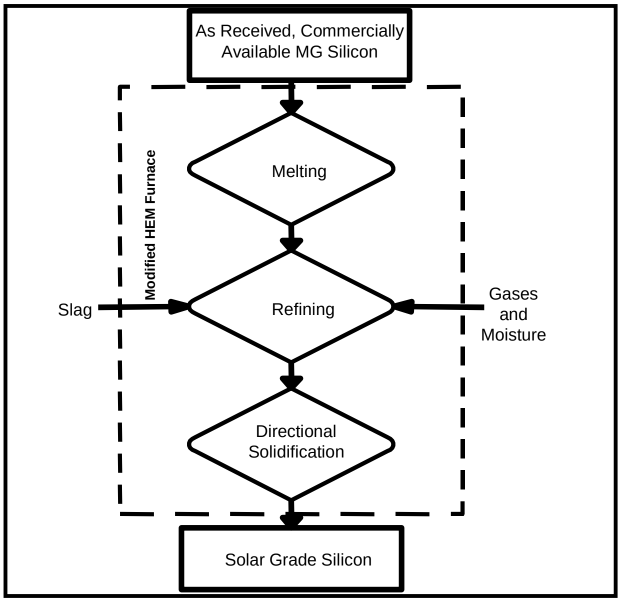

Figure 1. A schematic flow diagram of the approach to upgrade MG silicon to SoG silicon using HEM.

Element	ppmw	ppma	Element	ppmw	ppma
Li	<0.1	<0.40	As	0.16	0.06
B	0.13	0.34	Sr	0.069	0.02
F	<0.1	<0.15	Y	0.04	0.01
Na	0.048	0.059	Zr	0.073	0.022
Mg	0.006	0.007	Nb	0.03	0.009
Al	26	27	Mo	0.55	0.16
Si	Major	Major	Sn	<0.05	<0.01
P	11	10	Sb	<0.05	<0.01
S	0.095	0.083	Ba	<0.1	<0.02
Cl	0.55	0.44	La	<0.1	<0.02
K	0.022	0.016	Ce	0.13	0.03
Ca	5	3.5	Pr	<0.05	<0.01
Sc	<0.1		Nd	<0.05	<0.01
Ti	1.2	0.7	Sm	<0.05	<0.01
V	0.074	0.041	Eu	<0.05	<0.01
Cr	0.27	0.15	Gd	<0.05	<0.009
Mn	0.7	0.4	Tb	<0.05	<0.009
Fe	24	12	Dy	<0.05	<0.009
Co	0.13	0.06	W	<0.1	<0.015
Ni	0.65	0.31	Pb	<0.03	<0.004
Cu	0.11	0.05	Bi	<0.01	<0.001
Zn	<0.1	<0.04	Th	<0.01	<0.001
Ge	2.9	1.1	U	<0.01	<0.001

Figure 2. Impurity Analysis of a sample after refining commercially-available MG silicon showing B and P at 0.3 and 10 ppma, respectively.

The results showed (Figure 2) that using commercially-available MG silicon the B concentration can be reduced to about 0.3 ppma, well below the 1 ppma target for SoG silicon. The P concentration was reduced to about 7 ppma, and it will be necessary to reduce it further to <1 ppma. The experimental program has shown that this can be achieved using a slagging approach. In its current state this material cannot be used for solar cell application because it is P-rich (n-type) and most solar cell processes rely on a p-type (B-rich) substrate. For cell processes that can use compensated substrates the refining will have to stop earlier so that the net difference will be in favor of being B-rich (p-type). In summary, the refining processes developed for B reduction are compatible with the MG silicon production practices but a more effective P reduction process has to be developed to commercialize the direct production of SoG silicon from MG silicon for production of high efficiency solar cells.

Currently, large quantities of silicon scrap from the electronic industry are available that cannot be used for PV applications because of the very high B content. The B content of this silicon scrap is about 4 to 10 times that in MG silicon. However, aside from its B content, all other impurities are below levels required for SoG applications. The B reduction process has been used with this heavily B-doped silicon scrap from the electronic industry and reduced it to <1 ppma. This material has been used as feedstock using the Czochralski process and single crystals have been grown at NREL. These crystals have been fabricated[7] into high efficiency solar cells (13.4% efficiency) comparable to cells produced using electronic grade silicon feedstock (13.7% efficiency).

Of all processes for upgrading MG silicon, the B-reduction process discussed above is the simplest, most effective and most compatible with the processes and practices in an MG silicon production plant. It can be easily incorporated in an MG silicon plant for large-scale production at the lowest cost.

3. Conclusions

A low-cost B reduction process has been developed to remove B from commercially-available MG silicon and from heavily B-doped electronic scrap. Reducing the B concentration to <1 ppma for both types of feedstock is a technical breakthrough. This fundamental problem in the production of low-cost SoG silicon has been solved. It has been demonstrated that high-quality solar cells can be produced when the material is refined using this process.

4. References

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